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THERMAL DECOMPOSITION OF RDX AND RDX-BOROHYDRIDE MIXTURES

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U.S. ARMY LABORATORY COMMAND

BALLISTIC RESEARCH LABORATORY

ABERDEEN PROVING GROUND, MARYLAND

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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This report is a progress report on GCMS studies on the thermal decomposition of RDX, both alone and in mixtures with $K_2B_{12}H_{12}$. This work differs from previous work in that the less-volatile decomposition products are emphasized, rather than the gaseous products such as N_2O, $H_2C{=}O$, and NO. A number of these less-volatile products are formed. 1,3,5-triazine has been conclusively identified for the first time as a decomposition product of RDX. This is mechanistically significant because it suggests the operation of either some form of N-NO_2 cleavage or of intermolecular CH abstraction. Crude estimates of the effects on 1,3,5-triazine formation of temperature and of added $K_2B_{12}H_{12}$ have been made and are briefly discussed. Other products are still under study; those identified to date include mononitroso-RDX (MRDX) and unreacted RDX.

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I. INTRODUCTION

Very high burning rate (VHBR) propellants are needed for such applications as the monolithic charge and the traveling charge. These propellants generally contain RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and/or triaminoguanidine nitrate (TAGN) together with a borohydride such as one of the HIVELITES (Teledyne-McCormick-Selph). The borohydride greatly accelerates the burning rate of the propellant. The purpose of the present work is to elucidate the chemical mechanisms responsible for the burning rate acceleration, with the ultimate goal of optimizing propellant formulations for demonstration of the traveling charge concept, e.g., maximum "catalytic" effects with minimum sensitivity.

The approach employed involves gas chromatographic-mass spectroscopic (GC-MS) studies on the pyrolysis products of pure RDX and of RDX-$K_2B_{12}H_{12}$ mixtures. A number of previous studies (reviewed in References 2-7) have reported detailed analysis of the permanent gaseous products from decomposition of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and for RDX. The present work is concentrated mainly on the less-volatile products, namely those whose volatilities are intermediate between those of the more-commonly-studied permanently gaseous products on the one hand, and that of unreacted RDX on the other.

II. EXPERIMENTAL

RDX was obtained by crystallization of Class A military grade RDX from acetone. This reduced the HMX content from ca 5-10% to ca 0.3%. In an attempt to minimize particle-size effects, a portion of RDX was ground in a mortar for several minutes and divided into two portions, one of which was mixed with the $K_2B_{12}H_{12}$ and the other used in the uncatalyzed runs. Use of a set of standard seives showed that the average particle size was about 100μ. A sample of $K_2B_{12}H_{12}$ was obtained from Callery Chemical Company, Callery, Pennsylvania. The GC-MS experiments were carried out using a Hewlett-Packard (HP) 5890 gas chromatograph, with a HP 5970 mass-selective detector and a 59970B workstation consisting of a 9133 disk drive, 9100-236 computer and associated software (including library search software and complete NBS library of about 38,000 compounds), printer and plotter. The software is capable of producing complete spectra at any point, as well as either total ion chromatograms (plots of total-ion intensity vs. time), or ion chromatograms (plots of intensity vs. time for any particular ion or group of ions). Pyrolyses were carried out with a Chemical Data Systems (CDS) "Pyroprobe" pyrolyzer with coil probe, which was fitted to the injection port of the 5890 gas chromatograph by means of a heated interface, which was also obtained from CDS. The pyrolysis temperatures given are pyroprobe set temperatures.

In a typical run, an unweighed sample (ca 1 milligram) was put into a quartz tube 25 mm long having an inside diameter of 2 mm; the sample was retained in the tube with small plugs of quartz wool on either side. The sample was pyrolyzed by heating the probe to the desired temperature (given in the tables) with the fastest possible heating rate (ca 75°C/msec) and holding it there for 20 seconds. A split inlet was employed, with a split ratio of ca 30. The GC carrier gas was helium, with a flow rate through the column of ca 0.5 ml/min. Total flow was ca 40-45 ml/min, and the inlet purge flow was

ca 6 ml/min. The GC column was an HP-1 column (crosslinked methyl silicone gum, 12 m long, 0.2 mm i.d.; 0.3μm film thickness); the initial GC oven temperature was 70°C, for 3 minutes followed by heating at 20°C/minute to a final temperature of 210°C, followed by a final 5-minute hold time.

III. RESULTS

Chromatograms and mass spectra were obtained for decomposition of RDX alone, and for an RDX-$K_2B_{12}H_{12}$ mixture containing 19% $K_2B_{12}H_{12}$. Several runs were carried out at each of the following temperatures: 250, 400, 600 and 800°C. Typical chromatograms are shown in Figures 1-8.

Tables 1-4 include a summary of intensities of some of the more significant peaks in the spectra of 1,3,5-triazine formed in the decompositions. These tables represent series of runs carried out on the same day, all runs on a given day being carried out either with or without added $K_2B_{12}H_{12}$. An additional series of runs was carried out (Table 5), in which runs with and without added $K_2B_{12}H_{12}$ were alternated on the same day; it was hoped that this alternation of catalyzed and uncatalyzed runs on the same day would minimize differences between runs due to factors such as operator technique. The numbers in Tables 1-5 represent integrated total-ion intensities in the region 0-1 minute (Column 4), and integrated intensities of the single-ion intensities of the peaks at ca 0.5 minute in the single-ion chromatograms for m/e 44, 54, and 81. These were by far the most intense peaks in the chromatograms.

Figures 9a-9c are respectively the spectrum of a typical 1,3,5-triazine peak from the present work; the NBS library spectrum of 1,3,5-triazine; and the mass spectrum of an authentic sample of 1,3,5-triazine obtained on our apparatus.

Table 6 is a table of retention times for the most important peaks observed in the chromatograms of the products of the decomposition runs. The numbers in the "Figure" column of this table are those of the figures in the present report which give typical spectra for the respective peaks; these spectra are given in Figures 10-23. Note that many of the spectra in Figures 9-25 undoubtedly represent mixtures rather than pure components. This can be seen from some of the entries in Table 6, as well as from the baseline elevation in the 0.5-14 minute region of Figures 1-8.

Figure 24 is a chromatogram from heat-treatment of $K_2B_{12}H_{12}$ at 600°C; note that it contains two peaks, one at ca 0.4 minutes and the other at ca 6 minutes. Peak intensities increased with increasing temperature, as did the intensity of the second peak relative to the first. The 0.6 minute peak was identified from its mass spectrum as triethylamine, presumably remaining in traces from preparation of the $K_2B_{12}H_{12}$. The 0.4 minute peak remains unidentified. A typical mass spectrum of the 0.4 minute peak is shown in Figure 25; this spectrum resulted from decomposition at 800°C.

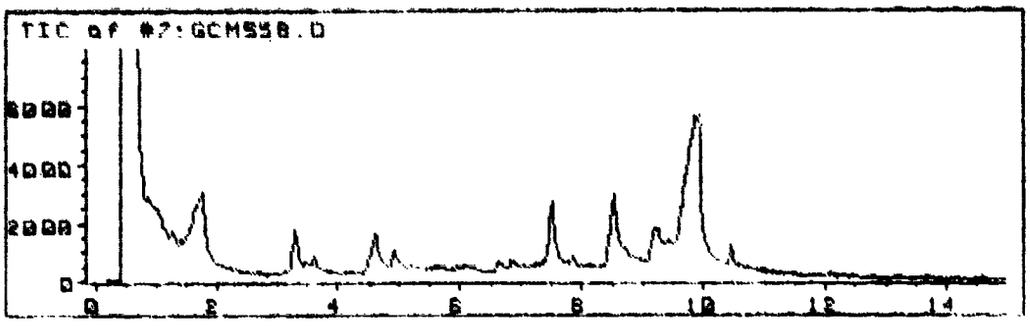


Figure 1. Total Ion Chromatogram from RDX Decomposed 20 sec at 250°C

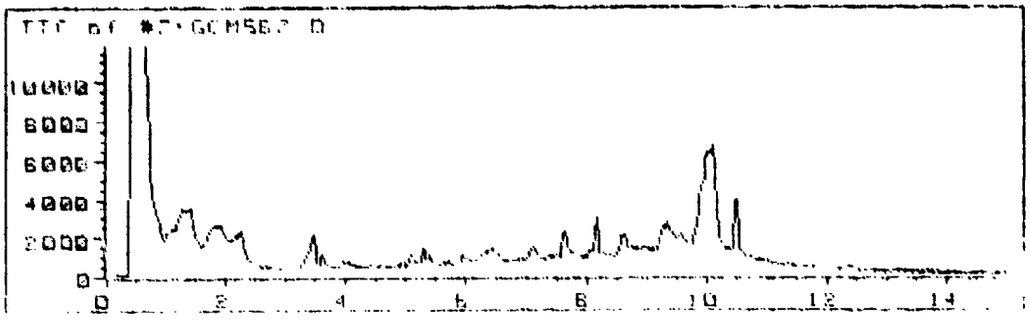


Figure 2. Total Ion Chromatogram from RDX + $K_2B_{12}H_{12}$ Decomposed 20 sec at 250°C

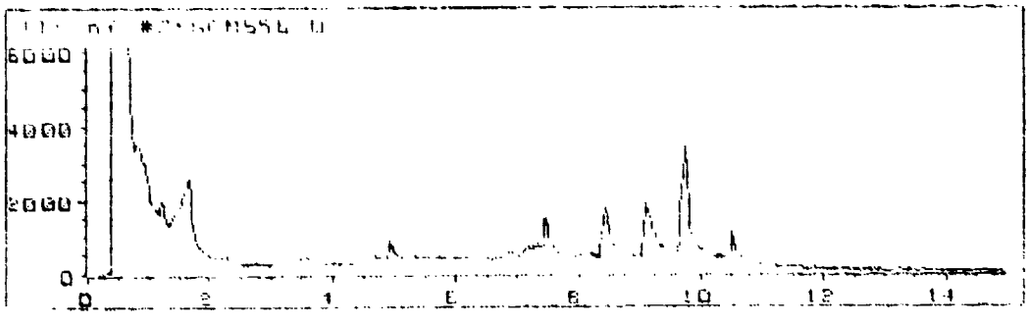


Figure 3. Total Ion Chromatogram from RDX Decomposed 20 sec at 400°C

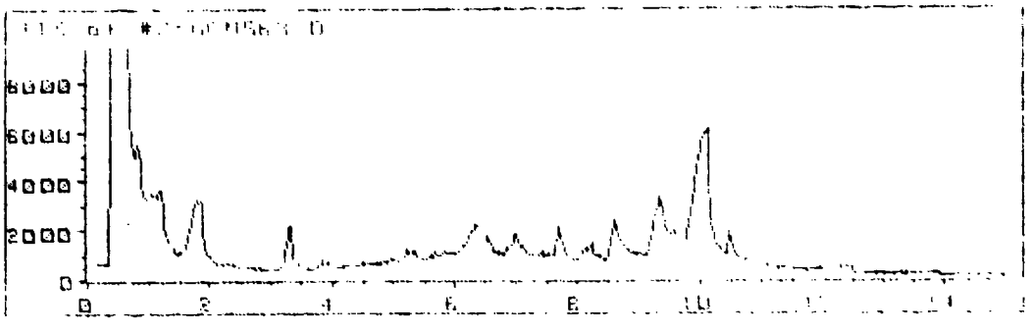


Figure 4. Total Ion Chromatogram from RDX + $K_2B_{12}H_{12}$ Decomposed 20 sec at 400°C

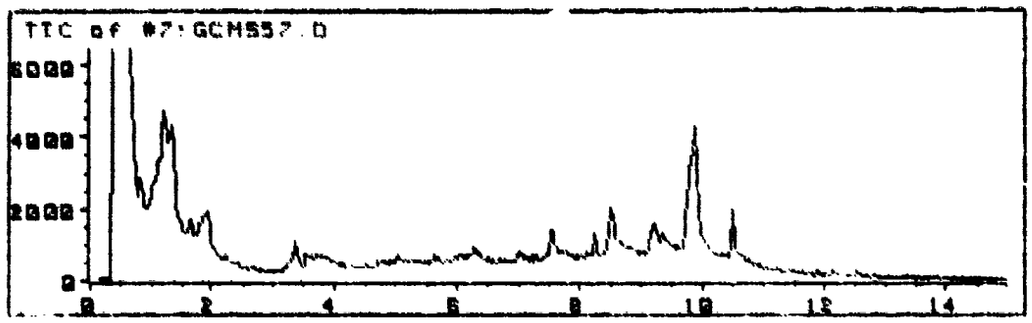


Figure 5. Total Ion Chromatogram from RDX Decomposed 20 sec at 600°C

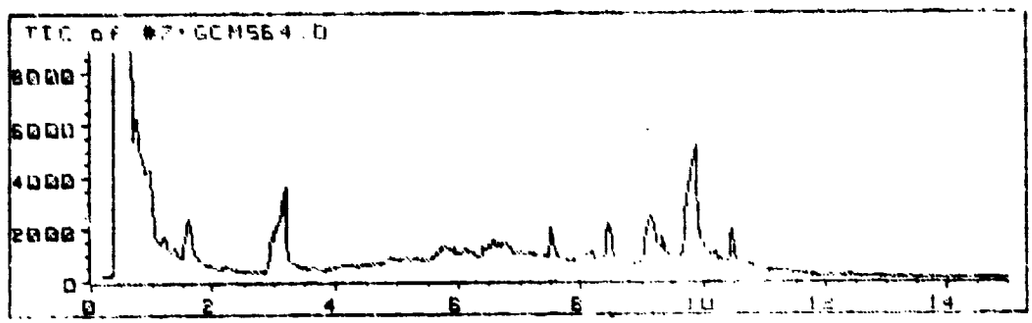


Figure 6. Total Ion Chromatogram from RDX + $K_2B_{12}H_{12}$ Decomposed 20 sec at 600°C

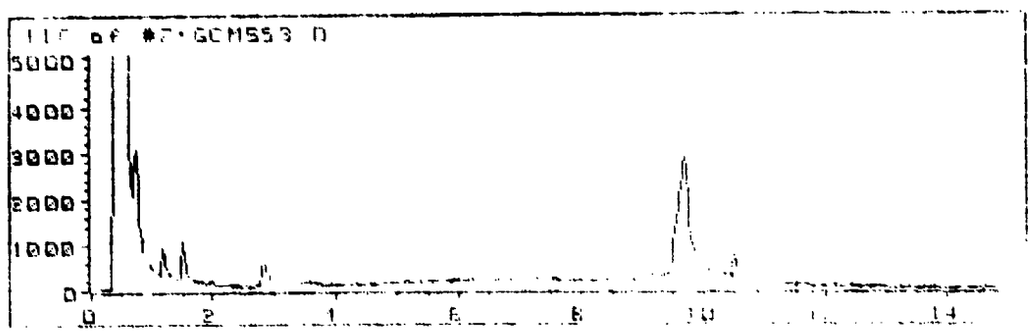


Figure 7. Total Ion Chromatogram from RDX Decomposed at 800°C

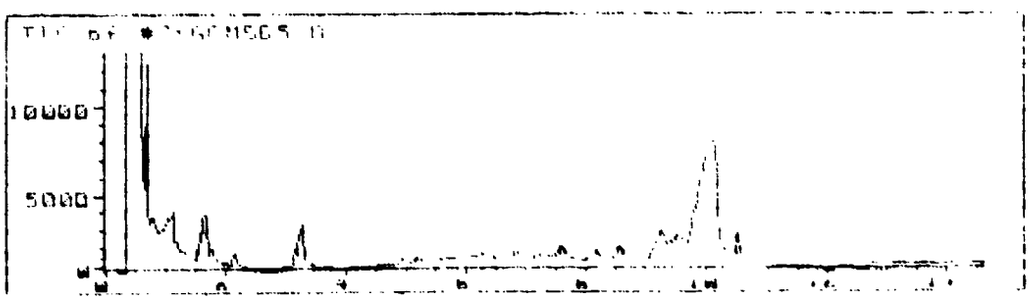


Figure 8. Total Ion Chromatogram from RDX + $K_2B_{12}H_{12}$ Decomposed 20 sec at 800°C

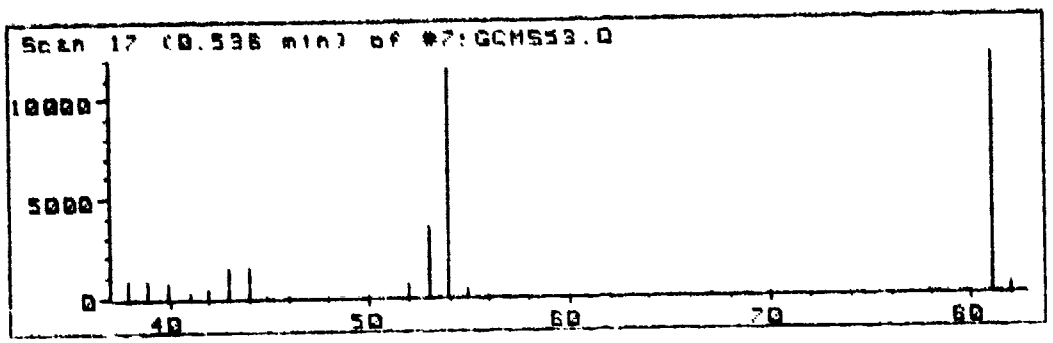


Figure 9a. Mass Spectrum of Peak from RDX Decomposed 20 sec at 800°C

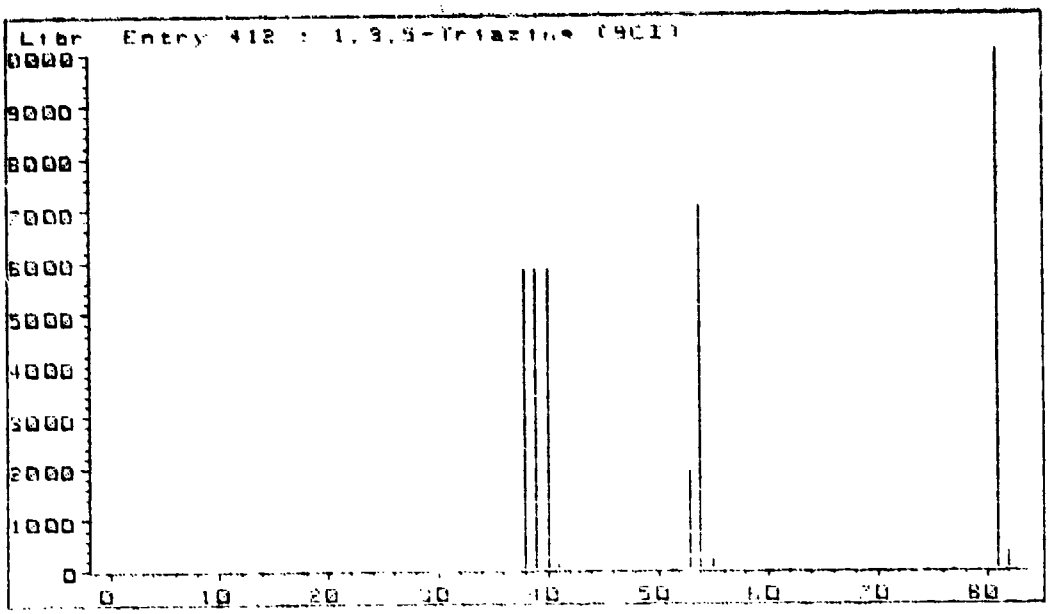


Figure 9b. NBS Library Spectrum of 1,3,5-Triazine

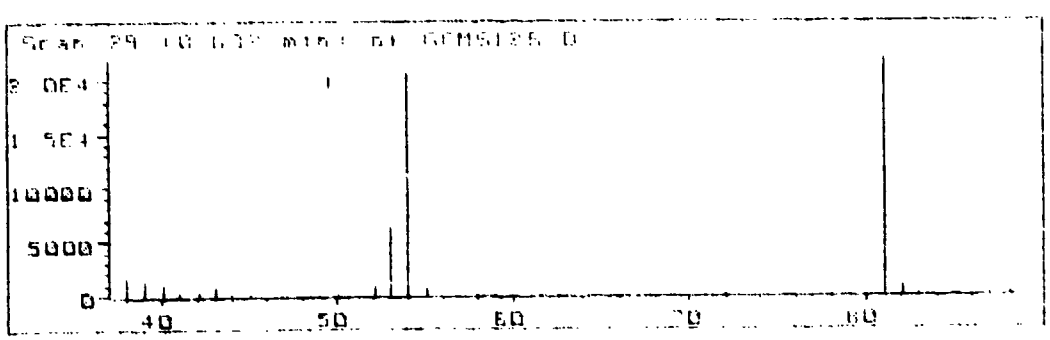


Figure 9c. Mass Spectrum of Authentic Sample of 1,3,5-Triazine, Run on the HP 5890-5970 MSD Used in the Present Work

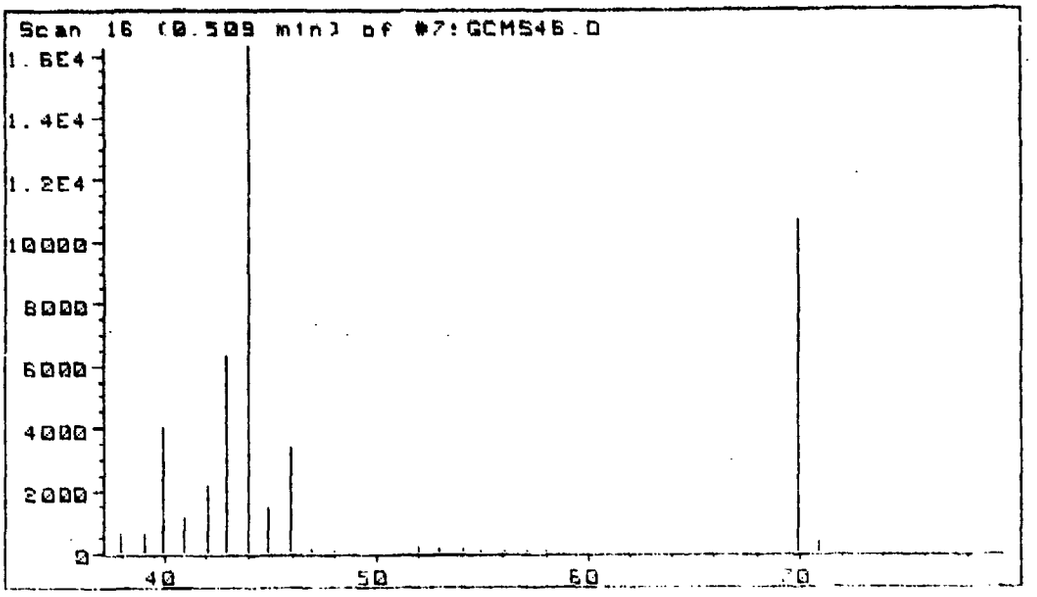


Figure 10. Mass Spectrum of Chromatographic Peak with Highest m/e = 70. The lines at m/e 44 and 46 are due to overlapping gaseous-product peaks.

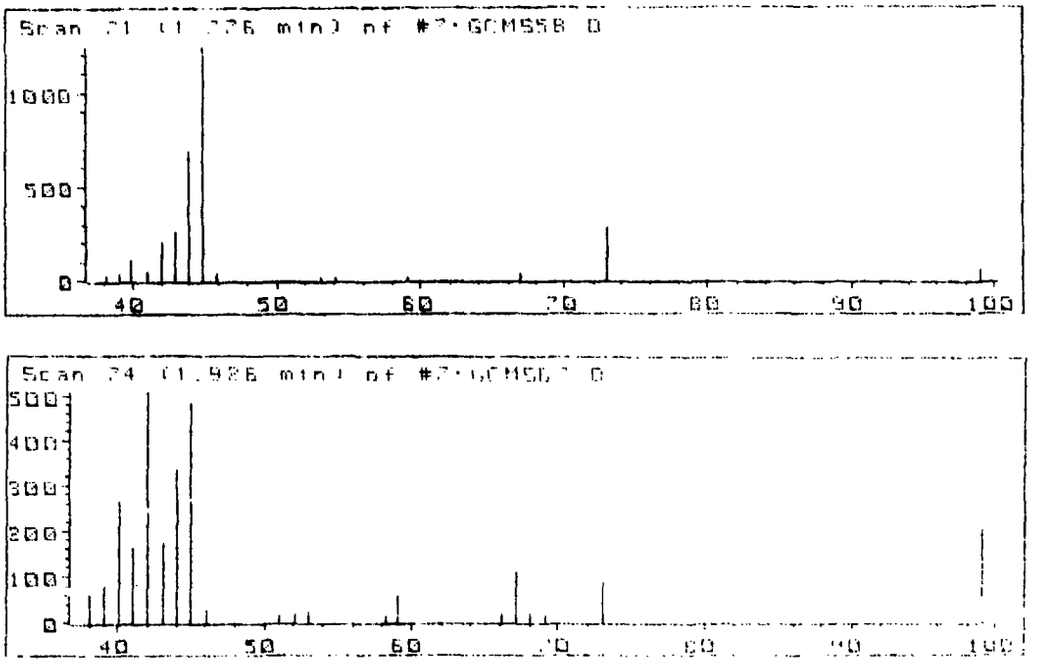


Figure 11. a. Typical Mass Spectrum of Chromatographic Peak at ca 1.7 Minute, RDX Alone Decomposed at 250°C. b. Same, RDX-$K_2B_{12}H_{12}$ Decomposed at 250°C.

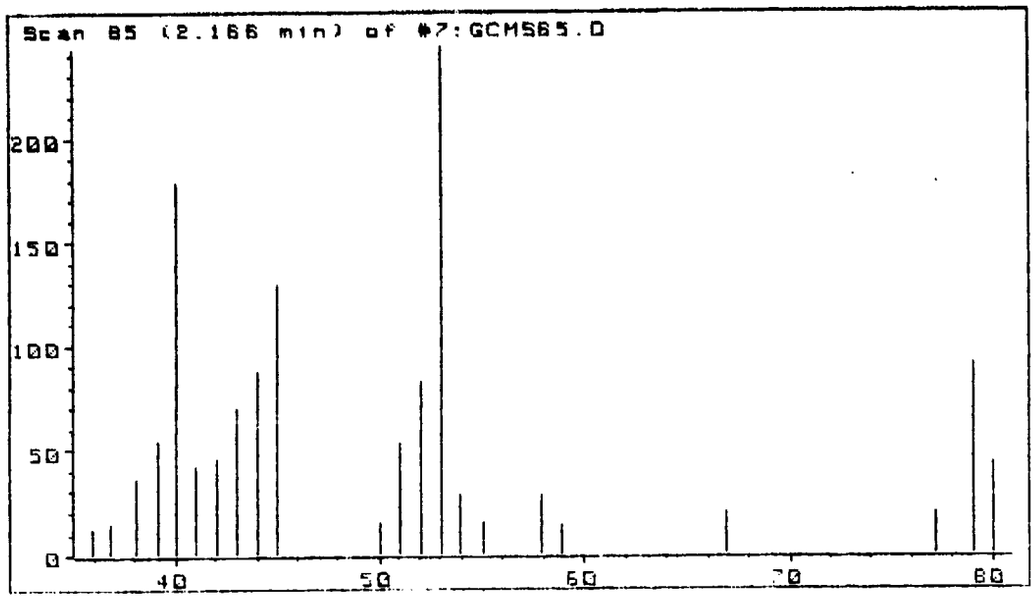


Figure 12. Typical Mass Spectrum of Chromatographic Peak at ca 2.1 Minutes

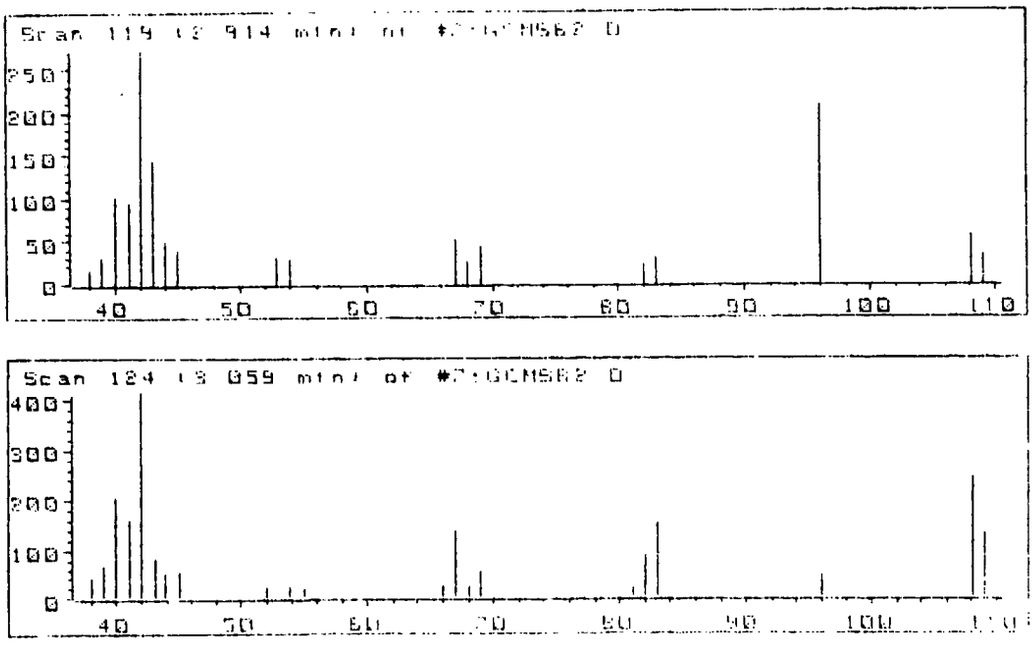


Figure 13. Typical Mass Spectra for Chromatographic Peak at ca 3.0 Minutes

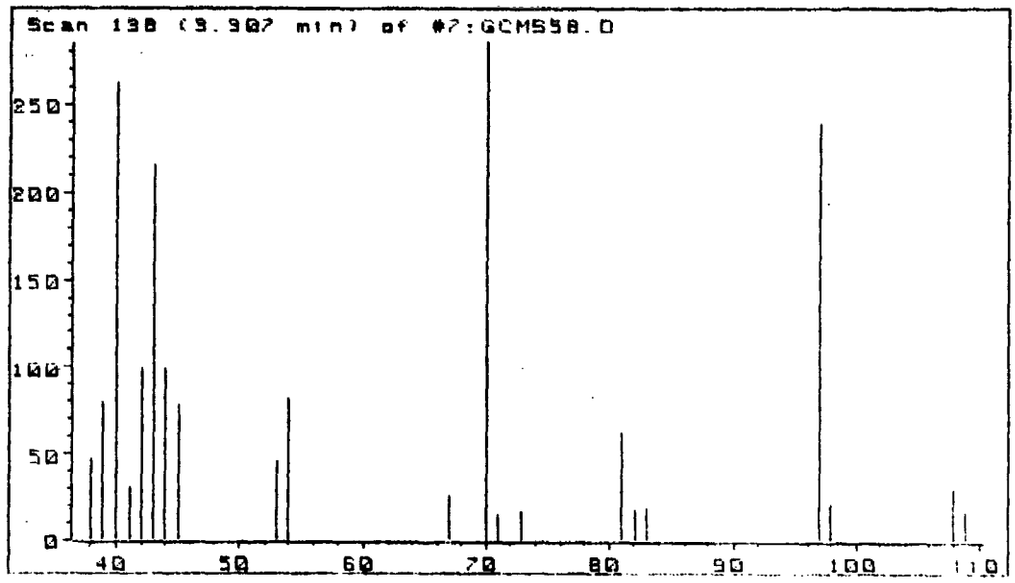


Figure 14. Typical Mass Spectrum of Chromatographic Peak Beleived to be 1,3,5-Triazine N-Oxide

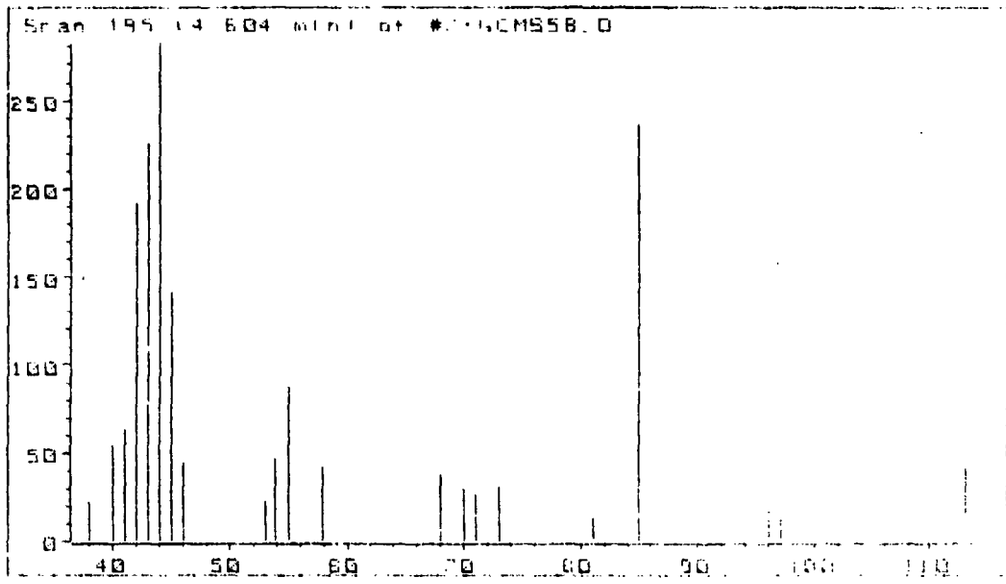


Figure 15. Typical Mass Spectrum of Chromatographic Peak at ca 4.6 Minutes

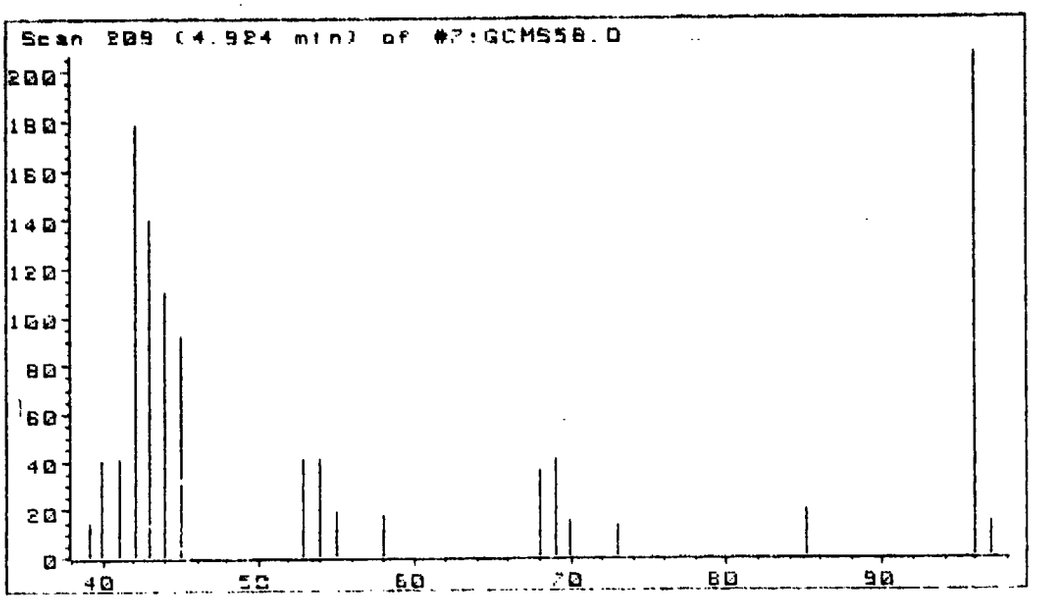


Figure 16. Typical Mass Spectrum of Chromatographic Peak at ca 4.9 Minutes

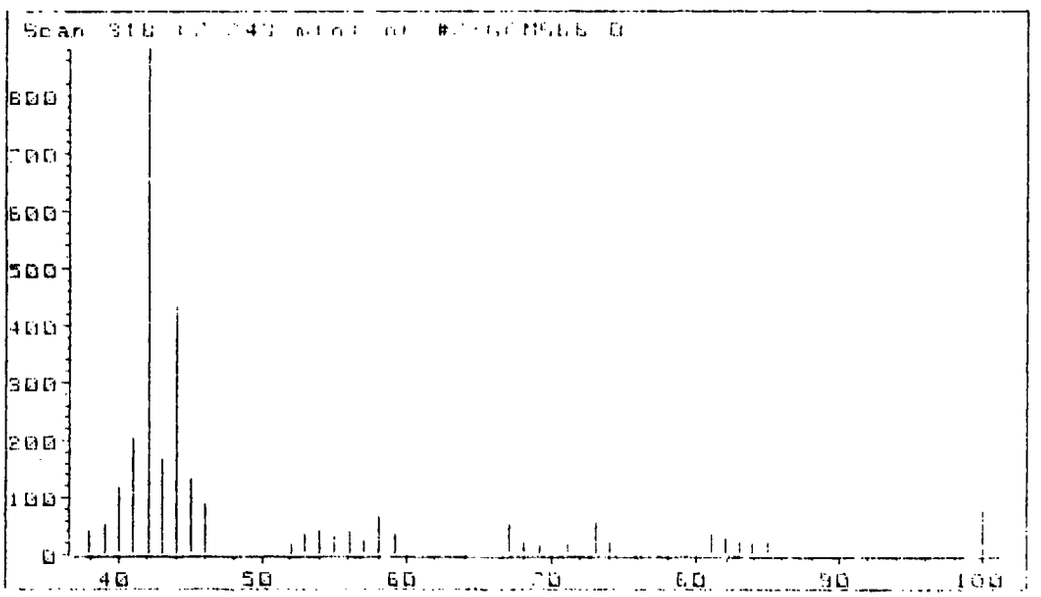


Figure 17. Typical Mass Spectrum of Chromatographic Peak at ca 7.5 Minutes

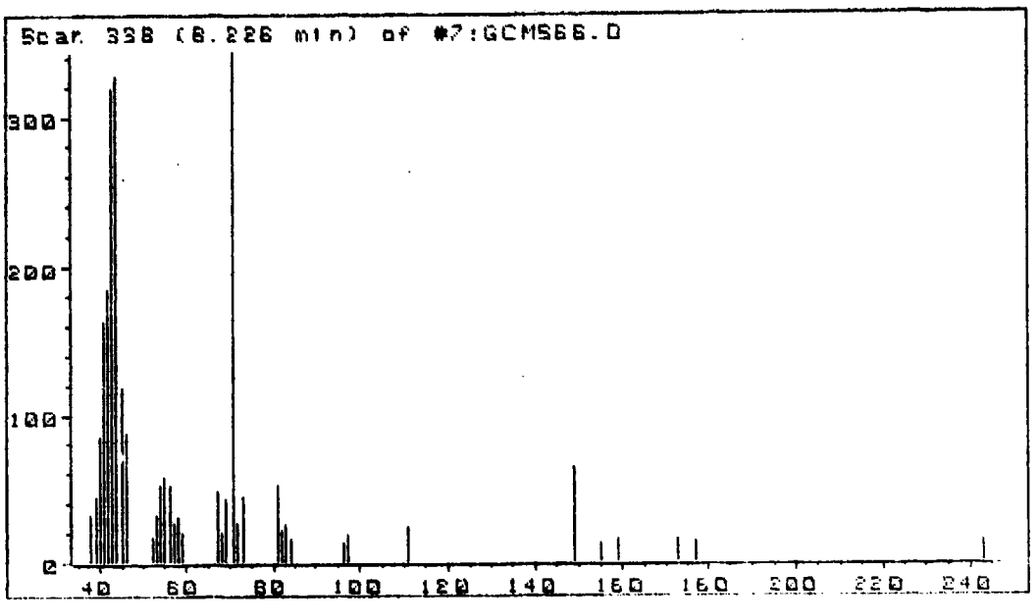


Figure 18. Typical Mass Spectrum of Chromatographic Peak at ca 8.2 Minutes

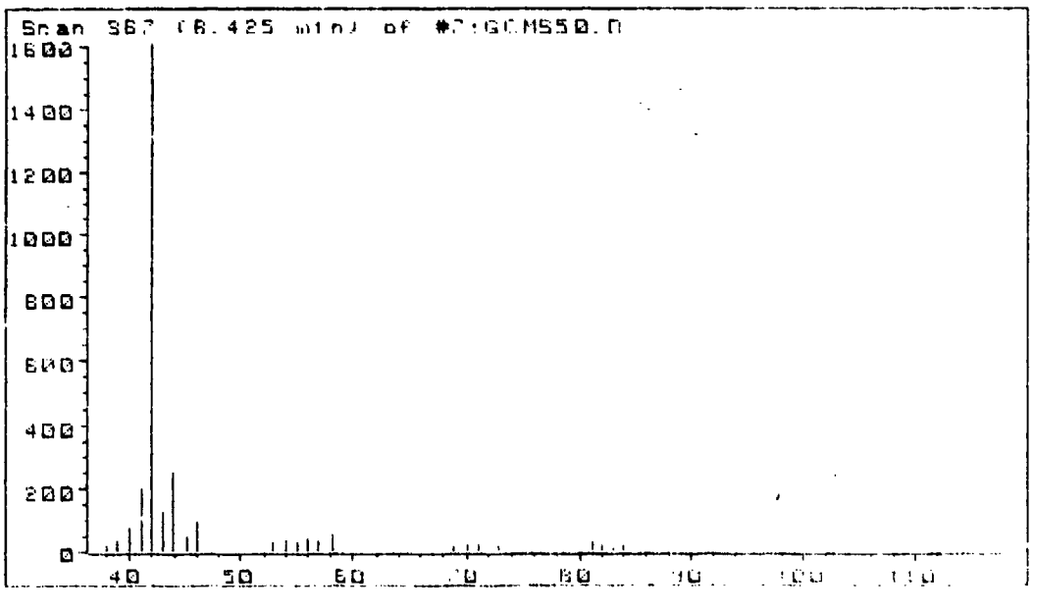


Figure 19. Typical Mass Spectrum of Chromatographic Peak at ca 8.6 Minutes

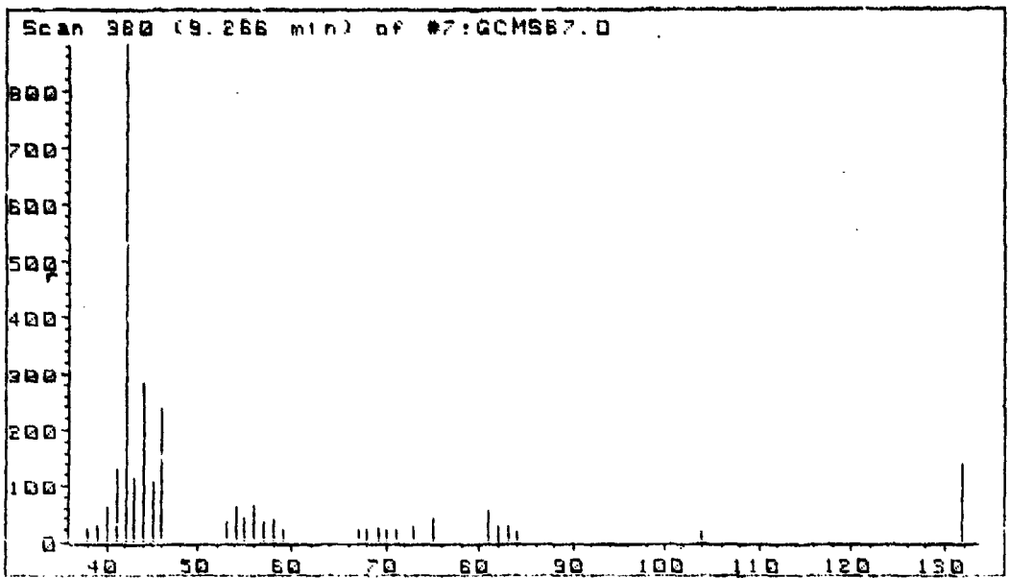


Figure 20. Typical Mass Spectrum of Chromatographic Peak at ca 9.2 Minutes

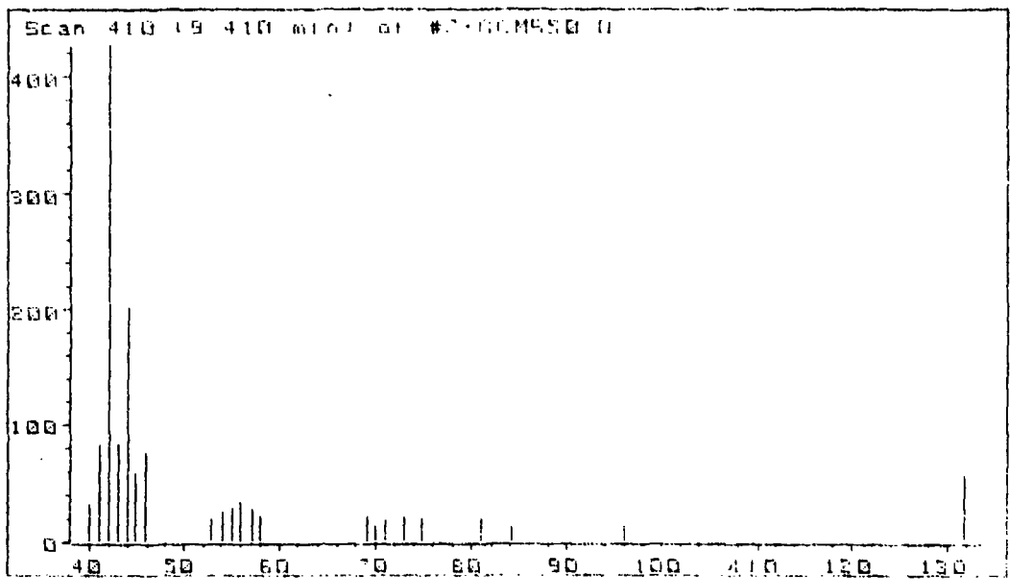


Figure 21. Typical Mass Spectrum of Chromatographic Peak at ca 9.4 Minutes

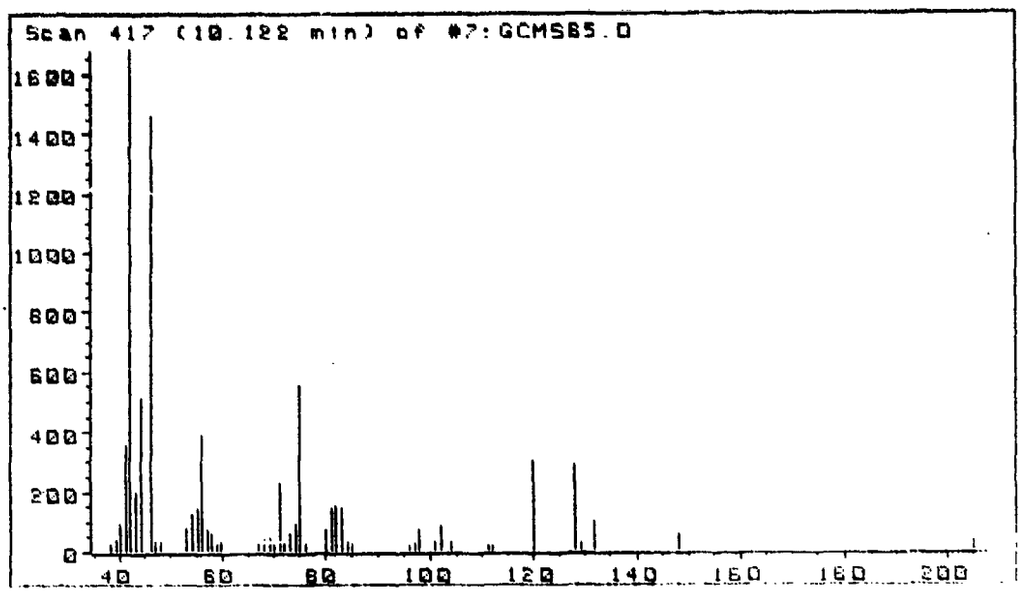


Figure 22. Typical Mass Spectrum of Chromatographic Peak at ca 9.9 Minutes

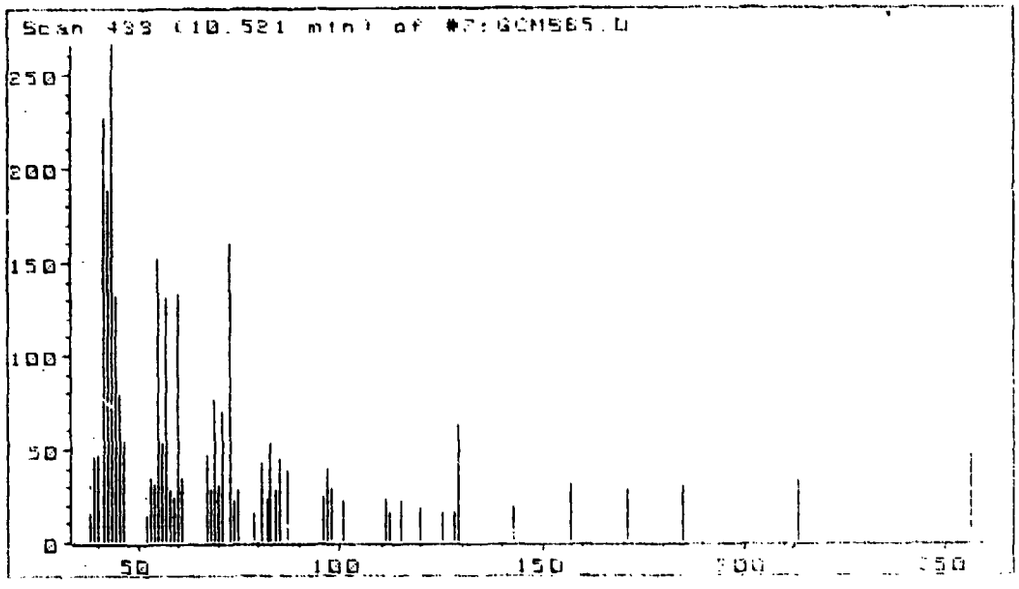


Figure 23. Typical Mass Spectrum of Chromatographic Peak at ca 10.5 Minutes

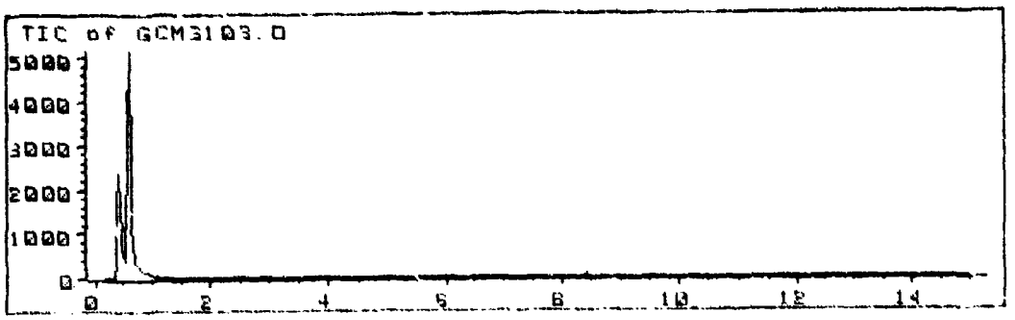


Figure 24. Typical Ion Chromatogram From $K_2B_{12}H_{12}$ "Decomposed" 20 sec at 600°C

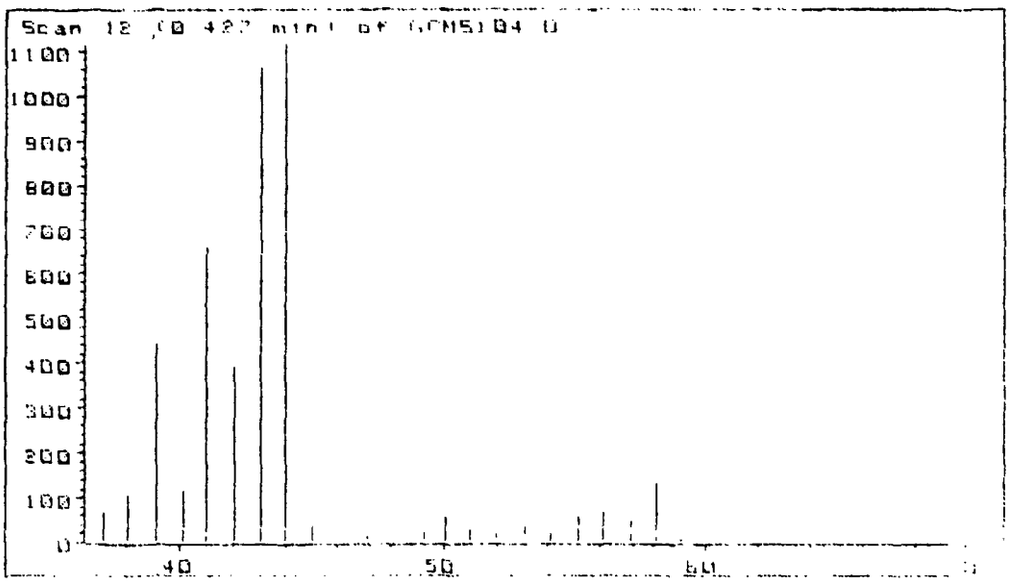


Figure 25. Typical Mass Spectrum of Chromatographic Peak at ca 0.4 Minutes from "Decomposition" of $K_2B_{12}H_{12}$ 20 sec at 800°C

Table 1. Areas and Area Ratios of Some Mass-Spectral Peaks in the Poorly-Retained Products, Pyroprobe at 250°C for 20 Seconds

Run	Date	Cat.?	Peak Areas ($x10^6$) at m/e				Area Ratios				
			Tot	44	54	81	44/Tot	54/Tot	81/Tot	54/44	81/44
46a	6/24/86	No	5.34*	2.85	0.161*	0.193*	0.534	0.0301*	0.0361*	0.0565*	0.0677*
50a	6/25/86	No	4.95*	2.89	0.357	0.404	0.584	0.0721	0.0816	0.124	0.140
58a	6/27/86	No	4.90*	2.56	0.341	0.389	0.522	0.0696	0.0794	0.133	0.152
72b	7/9/86	No	42.30	5.03	0.297*	0.338*	0.119	0.00702*	0.00799*	0.0590*	0.0672*
60a	7/1/86	Yes	5.98*	3.71	0.456	0.524	0.620	0.0763	0.0876	0.123	0.141
61a	7/1/86	Yes	4.49*	3.04	0.242	0.282	0.677	0.0539	0.0628	0.0796	0.0928
67a	7/2/86	Yes	6.58*	4.05*	0.345*	0.398*	0.615	0.0524*	0.0605*	0.0852*	0.0983*
74b	7/15/86	Yes	5.25*?	0.763	0.0658	0.0736	0.145	0.0125	0.0140	0.0862	0.0965
78b	7/15/86	Yes	11.56	1.753	0.0960*?	0.103*?	0.152	0.00830*?	0.00891*?	0.0548*?	0.0588*?

a - Masses 35-400 scanned
b - Masses 3-400 scanned
* - Complex (Two or more clear peaks)
*? - Slight Complexity (Shoulder or small second peak)

Table 2. Areas and Area Ratios of Some Mass-Spectral Peaks in the Poorly-Retained Products, Pyroprobe at 400°C for 20 Seconds

Run	Date	Cat.?	Peak Areas ($x10^6$) at m/e				Area Ratios				
			Tot	44	54	81	44/Tot	54/Tot	81/Tot	54/44	81/44
49a	6/24/86	No	5.25*	2.74	0.168*	0.194*	0.522	0.032*	0.0370*	0.0613*	0.0708*
51a	6/25/86	No	4.45*	2.25	0.214*	0.251*	0.506	0.0481*	0.0564*	0.0951*	0.112*
55a	6/26/86	No	5.72*	2.57	0.321*	0.372*	0.467	0.0561*	0.0650*	0.120*	0.139*
56a	6/27/86	No	4.83*	2.44	0.427	0.487	0.505	0.0884	0.101	0.175	0.200
71b	7/9/86	No	34.6	3.24$	0.700*?	0.798*?	0.0936	0.0202*?	0.0231*?	0.216*?	0.246*?
63a	7/1/86	Yes	5.81*	3.70$?	0.326*	0.363*	0.637	0.0561*	0.0625*	0.0881*	0.0981*
66a	7/2/86	Yes	7.82*	4.77$	0.405*	0.474*	0.610	0.0518*	0.0606*	0.0849*	0.0994*
75b	7/15/86	Yes	11.65	1.21	0.0642*	0.0721*	0.104	0.00549*	0.00619*	0.0531*	0.0596*

a - Masses 35-400 scanned
b - Masses 3-400 scanned
* - Complex (Two or more clear peaks)
*? - Slight Complexity (Shoulder or small second peak)
$ - Slightly flat-topped peak

Table 3. Areas and Area Ratios of Some Mass-Spectral Peaks in the Poorly-Retained Products, Pyroprobe at 600°C for 20 Seconds

Run	Date	Cat.?	Peak Areas ($x10^6$) at m/e				Area Ratios				
			Tot	44	54	81	44/Tot	54/Tot	81/Tot	54/44	81/44
52a	6/25/86	No	4.56*	1.95	0.484	0.529	0.428	0.106	0.116	0.248	0.271
57a	6/27/86	No	6.58*	2.62	0.767	0.826	0.398	0.117	0.126	0.298	0.316
70b	7/9/86	No	59.71	4.20	1.31	1.46	0.0703	0.0219	0.0245	0.312	0.398
64a	7/2/86	Yes	6.72*	3.60	0.665	0.759	0.536	0.0990	0.113	0.185	0.211
68a	7/2/86	Yes	7.91*	3.89	0.731	0.828	0.492	0.0924	0.105	0.188	0.213
76b	7/15/86	Yes	14.56*	1.33	0.127*?	0.135*?	0.0913	0.00872*?	0.00927*?	0.0954*?	0.102*?

a - Masses 35-400 scanned
b - Masses 3-400 scanned
* - Complex (Two or more clear peaks)
*? - Slight Complexity (Shoulder or small second peak)

Table 4. Areas and Area Ratios of Some Mass-Spectral Peaks in the Poorly-Retained Products, Pyroprobe at 800°C for 20 Seconds

Run	Date	Cat.?	Peak Areas ($x10^6$) at m/e				Area Ratios				
			Tot	44	54	81	44/Tot	54/Tot	81/Tot	54/44	81/44
53a	6/25/86	No	4.045*	1.90	0.391	0.430	0.470	0.0967	0.107	0.205	0.226
54a	6/26/86	No	5.07*	2.34	0.429	0.483	0.462	0.0846	0.0953	0.183	0.206
59a	6/27/86	No	3.69*	2.09	0.150	0.177	0.566	0.0406	0.0480	0.0718	0.0847
69b	7/9/86	No	44.46	4.31	0.646	0.722	0.0969	0.0145	0.0162	0.150	0.168
73b	7/9/86	No	50.00	4.90	0.704	0.784	0.0980	0.0141	0.0157	0.144	0.160
62a	7/1/86	Yes	5.34*	3.11	0.383	0.417	0.582	0.0717	0.0781	0.123	0.134
65a	7/2/86	Yes	6.76*	3.78	0.525	0.587	0.559	0.0777	0.0868	0.139	0.155
77b	7/15/86	Yes	16.11*?	1.29$?	0.124	0.134	0.0801	0.00770	0.00832	0.0961	0.104

a - Masses 35-400 scanned
b - Masses 3-400 scanned
* - Complex (Two or more clear peaks)
*? - Slight Complexity (Shoulder or small second peak)
$ - Slightly flat-topped peak

Table 5. Effect of Alternating Catalyzed and Uncatalyzed Runs on Areas and Area Ratios of Some Mass-Spectral Peaks in the Poorly-Retained Products

Run	Date	Cat.?	Temp	Peak Areas ($x10^6$) at m/e				Area Ratios				
				Tot	44	54	81	44/Tot	54/Tot	81/Tot	54/44	81/44
31a	5/16/86	Yes	600	1.25*	1.02	Present	Present	0.816	-----	----	----	----
32a	5/16/86	No	600	8.08*	4.59	0.68	0.82	0.568	0.084	0.10	0.15	0.18
33a	5/16/86	Yes	600	6.04*	4.50	0.20	0.26	0.745	0.033	0.043	0.044	0.058
34a	5/16/86	No	600	2.25*	1.24	0.169	0.20	0.551	0.0751	0.089	0.136	0.16
35a	5/20/86	Yes	600	12.92	7.79	0.71	0.82	0.603	0.055	0.064	0.091	0.11
36a,b	5/20/86	No	600	11.80	7.26	0.755	0.953	0.621	0.0639	0.0808	0.104	0.131
43a	6/19/86	Yes	600	5.66*	2.42	0.49	0.52	0.428	0.0866	0.0919	0.202	0.21
44a	6/19/86	No	600	4.36*	1.65	0.44	0.49	0.378	0.101	0.112	0.267	0.30
45a	6/19/86	Yes	600	5.33	2.44	0.48*?	0.51*?	0.458	0.090*?	0.096*?	0.197*?	0.209*?
23a,c	5/13/86	Yes	250	8.08*	4.76	0.207*	0.237*	0.589	0.026*	0.029*	0.043*	0.050*
25a,d	5/13/86	No	250	9.15*	5.44	0.225*	0.265*	0.594	0.025*	0.029*	0.041*	0.049*
27a,e	5/14/86	Yes	250	11.30*	7.24	0.247*	0.269*	0.641	0.022*	0.024*	0.034*	0.037*
29a,c	5/14/86	No	250	6.83*	3.65	0.319*	0.366*	0.534	0.047*	0.054*	0.087*	0.100*

a - Masses 35-400 scanned
b - Atypical run - helium leak caused broad peaks and long retention times
c - Fresh tube
d - Tube used for run 23, probably contaminated with $K_{12}B_{12}H_{12}$ residue, therefore not a typical uncatalyzed run
e - Tube used for runs 23-25
* - Complex (Two or more clear peaks)
*? - Slight Complexity (Shoulder or small second peak)

Table 6. Table of Peaks in Total Ion Chromatograms from RDX and RDX-$K_2B_{12}H_{12}$ Decompositions

Time (minutes)	Occurrence	Spectrum (Figure)	Remarks
ca 0-1	All Conditions	9a (Triazine) 10 (Oxadiazole(?))	Includes permanent gases (N_2O, CO_2), 1,3,5-triazine and a peak with highest mass at m/e 70 (1,2,4-oxadiazole?)
ca 1-2.5	All Conditions	1-8*	Especially at low temperatures, this region is difficult to characterize. It sometimes includes broad, variable peaks whose spectra resemble formamide.
1.7±0.2	All Conditions	11	Appears under all conditions. Looks like a mixture. A: Highest mass = 99. B: Highest mass = 73. Is B HC(=O)NHC(=O)H or Dimethylformamide?
2.1	High-T Cat.	12	Sometimes present at high temperature, from decomposition with added $K_2B_{12}H_{12}$.
3.0±0.4	All Conditions	13	Spectrum shows this is not 1,3,5-triazine N-oxide. Present under all conditions, especially at high temperature with added $K_2B_{12}H_{12}$. Looks like a mixture. A: Highest mass = 108/109. B: Highest mass = 96.
3.3	Low-T Uncat.	14	1,3,5-Triazine N-oxide (tentative). Sometimes appears at low (250°C) temperature for RDX alone; not seen at higher temperatures or with added $K_2B_{12}H_{12}$.
4.6	Low-T Uncat.	15	From decomposition at low (250, 400 C) temperature, without added $K_2B_{12}H_{12}$.

Table 6. Table of Peaks in Total Ion Chromatograms from RDX and RDX-$K_2B_{12}H_{12}$ Decompositions (CONT'D)

Time (minutes)	Occurrence	Spectrum (Figure)	Remarks
4.9	Low-T Uncat.	16	From some decomposition runs at low (250, 400°C) temperature, without added $K_2B_{12}H_{12}$.
ca 5-7	All	1-8*	This region included a number of weak peaks, especially from decomposition at low (250, 400°C) temperature, with added $K_2B_{12}H_{12}$. A peak with m/e 58 is sometimes seen at ca 6.5 min; is this hydroxymethylformamide - OH?
7.6±0.1	Catalyzed; Low-T Uncat.	17	Not reproducible. Usually highest m/e = 100, sometimes 110, 114, 149 or 177. Not seen for RDX alone at high temperature.
8.2	Catalyzed	18	Sometimes occurs, especially in presence of $K_2B_{12}H_{12}$. Does this contain B_4 fragments?
8.6±0.1	Catalyzed; Low-T Uncat.	19	Not seen for RDX alone at high temperature.
9.2±0.2	All Conditions	20	Occurs under most conditions, even weakly at high (800°C) temperature. Has m/e 132; beleived to be MRDX.
9.4±0.1	All Conditions	21	Occurs under most conditions, even weakly at high (800°C) temperature. Has m/e 132; is this DRDX?
9.9±0.2	All Conditions	22	Unreacted RDX; always present regardless of temperature or presence of $K_2B_{12}H_{12}$.
10.5	All Conditions	23	Often present regardless of temperature or presence of borohydride.

*Total Ion Chromatogram.

IV. DISCUSSION

A. Identification of Chromatographic Peaks

Figures 1-8 show total ion chromatograms for typical catalyzed and uncatalyzed runs carried out at 250, 400, 600 and 800°C. The more important chromatographic peaks are tabulated in Table 6 and their spectra are shown in Figures 10-23. Even under similar conditions of temperature and presence/absence of catalyst, some variations in presence and intensity of cetain peaks were seen. However these chromatograms are typical of those obtained under the conditions in question. Identification of the various peaks in these complex systems is still in progress, and at present many peaks remain unidentified. Some complete and partial identifications are discussed below. Some apparent patterns in effect of catalysis and temperature on the relative degree of formation of 1,3,5-triazine, one of the more mechanistically significant products formed, are then discussed briefly.

Note that, in these chromatograms, the relatively very intense peak(s) at the beginning of the chromatogram (retention time ca one-half minute) correspond to the gaseous products[1-5] (N_2O, formaldehyde, CO, CO_2, N_2, etc.), that are examined in most studies[1-7] on HMX and RDX decomposition, while the weaker peaks following it are due to less-volatile products, with retention strengths approximately intermediate between those of the permanent gaseous products and unreacted RDX.

Unreacted RDX. Other than the gaseous-product peak at ca 0.5 minute, the most intense peak in the chromatograms shown in Figures 1-8 occurs at ca 9.8-10 minutes. This peak is identified as unreacted RDX by comparison of its mass spectrum with a reference spectrum contained in the NBS library (Table 6, Figure 22).

1-Mononitroso-3,5-dinitro-hexahydro-1,3,5-triazine (mononitroso-RDX, MRDX). The peak at ca 9.15 ± 0.2 minutes (Table 6, Figure 20) is tentatively identified as MRDX, based on comparison of its mass spectra and retention times with those obtained by injection of an acetone solution of an authentic sample of a mixture of MRDX and DRDX; the author thanks Professor T.B. Brill for furnishing this sample. The question of the presence of dinitroso-RDX (DRDX) and trinitroso-RDX among the decomposition products is still under investigation. Nitrosoamines have been detected previously in HMX and RDX decomposition,[4-6,8,9,10] especially in the liquid phase and in solution.

Formamide, $HC(=O)NH_2$. A number of the decomposition runs gave spectra closely resembling that of formamide for a peak in the 0.8-1.3 minute region. Non-pyrolytic injections of an authentic sample of formamide suggest that its retention time on the column used is in this region, and can be quite broad. However this identification should be considered uncertain due to the spread in retention times and the observation of extra (impurity?) ion-fragments in the mass spectra of the peaks in question.

1,3,5-Triazine. A number of runs gave computer-run NBS library searches in which one of the best matches for a peak at ca 0.6 minutes was 1,3,5-triazine; see for example Figure 9a. The three peaks at m/e 38, 39, and 40 are weaker in our spectrum (Figure 9a) than in the NBS spectrum (Figure 9b). This possible source of uncertainty was resolved by injecting an authentic

sample of 1,3,5-triazine into our apparatus (Figure 9b); this also showed weaker peaks at m/e 38, 39, and 40. Thus it seems reasonable to conclude that the above intensity difference is due to variations between our 5970 MSD and the spectrometer that was used to record the authentic spectrum contained in the NBS library and reproduced in Figure 9c. Even though not all runs showed a separate peak at this point on their respective total-ion chromatograms, all did have selected ion chromatograms showing reasonably strong peaks at ca 0.6 min for m/e 81 (parent peak of 1,3,5-triazine) and m/e 54 (parent-HCN). It therefore seems reasonable to conclude that under these conditions, 1,3,5-triazine is formed in every run. Furthermore, peak shapes for the peaks at m/e 54 and 81 were identical within a given run; this suggests that these ion-chromatogram peaks came through the column in the same compound.

Peaks in the mass spectra of decomposing RDX and HMX have previously been attributed[12,13] to 1,3,5-triazine and closely related species. Also, 1,3,5-triazine has been detected from ir multiphoton dissociation of RDX in a molecular beam.[14a] However, the present work is apparently the first report of its separation and identification by chromatographic techniques.

Additional Compounds Possibly Present. Several additional compounds are at least suggested by the mass spectra of various chromatographic peaks, but without authentic samples or at least spectra on hand, it is hard to be sure. These compounds include dimethylformamide, $HC(=O)-N(CH_3)_2$; oxadiazole derivative (five-membered cyclopentadieneoid ring containing two nitrogens and one oxygen); and 1,3,5-triazine N-oxide.

The 1,3,5-triazine oxide peak was seen in the absence of $K_2B_{12}H_{12}$ at 250°C, but was greatly reduced or eliminated at higher temperatures and in the presence of $K_2B_{12}H_{12}$. Note also that detection of 1,3,5-triazine oxide would be in agreement with detection of peaks at m/e 97 and 98 in atmospheric pressure chemical ionization studies[11] on RDX decomposition which have been carried out at CRDEC.

The peaks of almost equal intensity at m/e 43 and 44 in the 8.2 minute peak (Figure 18) and in the 0.4 minute peak from $K_2B_{12}H_{12}$ at 800°C (Figure 25) seem at least consistent with the presence of B_4 fragments.[14b]

B. Preliminary Observations Concerning Catalyst and Temperature Effects on Formation of 1,3,5-Triazine

Columns 4-7 of Tables I-IV contain summaries of integrated total intensities of the almost-unretained (retention time less than ca 0.8 minute) products, as well as of the peaks corresponding to m/e 44 (believed to be mostly CO_2 and N_2O), 54 and 81 (the two strongest peaks in the mass spectrum of 1,3,5-triazine, see Figure 9.). The last five columns of Tables 1-4 contain the ratios of the areas of the peaks m/e 44, 54 and 81 to the total ion area, and of the integrated areas of the m/e 54 and 81 ions to the m/e 44 ion. The purpose of the ratioing was to compensate at least partially for the fact that the samples were unweighed, thereby obtaining at least a crude normalized estimate of the relative amounts of 1,3,5-triazine formed in the various runs. This seemed worthwhile because of the possible mechanistic significance of the formation of 1,3,5-triazine. Note however the possibility

of uncertianty due to such factors as changes with temperature or degree of catalysis in the relative amounts of the gaseous products.

General Considerations. The portion (ca 0-0.8 minute) of the total ion chromatogram corresponding to the almost-unretained products often showed several peak maxima, apparently due to the presence of several different products. These runs are indicated by an asterisk adjacent to the number in column 4 (Tables 1-4) or 5 (Table 5).

Furthermore, the peaks at ca 0.6 minute in the ion chromatograms for m/e 54 and 81 (strongest peaks in the mass spectrum of 1,3,5-triazine) were often complex, exhibiting a shoulder or even two distinct peaks. Peaks exhibiting this behavior are indicated by an asterisk next to the numbers in columns 6 and 7 (Tables 1-4) or 7 and 8 (Table 5). This complexity occurred most often in the runs carried out at the two lowest temperatures (250 and 400°C.), and often appeared to parallel reduced yields of 1,3,5-triazine (m/e 54 and 81) relative to total products and m/e 44. The reasons for this behavior are not understood. Possible explanations include: (a) Vaporization of some RDX out of the quartz tube, followed by condensation on the walls of the interface in which the pyroprobe is inserted and/or the ends of the tube, and further decomposition of the condensate, resulting in two spurts of gaseous decomposition products. This seems unlikely, however, since the interface was maintained at 150°C, a temperature at which decomposition should be too slow to give a second spurt of decomposition products only a few seconds behind the first. A second possibility might be (b) sequential formation of 1,3,5-triazine by two different decomposition mechanisms, resulting in two spurts of 1,3,5-triazine; however there is no evidence for this. A third possibility involves (c) decomposition of different portions of the sample at different times, due to uneven distribution of the sample in the tube. This does not seems unreasonable, in view of the length of the pyrolysis event (20 seconds or even more, since there was undecomposed material remaining in the tube after the 250 degree decompositions), compared to the time (several seconds) between the two portions of the split peak. The reduced amounts of 1,3,5-triazine formed in runs with complex m/e 54 and 81 peaks could possibly be explained in terms of (a) or (c) if the triazine is formed at least partially in a bimolecular reaction of unreacted RDX with a decomposition product, since such reactions might be expected to be less important if the sample is small or highly dispersed.

The m/e 54 and 81 peaks marked with asterisks in the tables were not considered in preparing the following discussion, since it was felt that they might not be comparable with the runs whose m/e 54 and 81 peaks were relatively well-behaved. In a few cases, asterisked peaks whose complexity seemed only slight are marked with a question mark next to the asterisk; these peaks were considered but given less weight.

The m/e 44 peaks seem fairly well-behaved; in only a very few cases are there any complexities or odd-shaped peaks. Furthermore, the area ratios between these peaks and the total ion intensities show much less variation for a given temperature and degree of catalysis than do the m/e 54 and 81 peaks. This indicates that the mass spectrometer and associated computers and integrating software are functioning properly, and that the apparent unruly behavior of the 1,3,5-triazine peaks at m/e 54 and 81 is not due to instrument malfunction or to operator error.

Effect of Catalyst on Relative Intensities of m/e 44 and 1,3,5-Triazine Peaks. If the asterisked m/e 54 and 81 peaks are dropped from consideration, it appears (Tables 1-5) that addition of $K_2B_{12}H_{12}$ as a catalyst causes (a) an increase in relative amount of m/e 44 (N_2O and CO_2), and (b) a decrease in relative amount of 1,3,5-triazine formed. These conclusions follow from the last five columns of the tables, which show area ratios for the m/e 54 and 81 peaks to the total intensity and to the intensity of the m/e 44 peak, and for the m/e 44 peak to the total intensity. There are some exceptions, for example run 59 (Table 4) is an exception to both correlations and run 77, also in Table 4, is an exception to (a). The amount of change caused by adding the $K_2B_{12}H_{12}$ also seems to vary from run to run, being for example negligible in run 60 but significant in run 61 (Table 1). Nevertheless, based on the preponderance of the data in Tables 1-5, it seems reasonable to draw conclusions (a) and (b).

Effect of Temperature on Relative Intensities of m/e 44 and 1,3,5-Triazine Peaks. Increasing the decomposition temperature between 250°C and 600°C causes a decrease in the relative amount of m/e 44 and an increase in the relative amount of the 1,3,5-triazine peaks (m/e 54 and 81); but these trends are not continued on increasing temperature further, to 800°C. In the 250-600 degree range this is in agreement with previous work[4,6,7] which suggests that the amount of products such as N_2O, N_2 and H_2CO decreases with increasing decomposition temperature, while the yields of products such as HCN, NO and NO_2 increase. Possible explanations for failure of the trends to continue to the 800°C region include temperature-induced shifts[4] in the composition and/or amount of decomposition products, or thermal decomposition of 1,3,5-triazine at temperatures above 600°C.

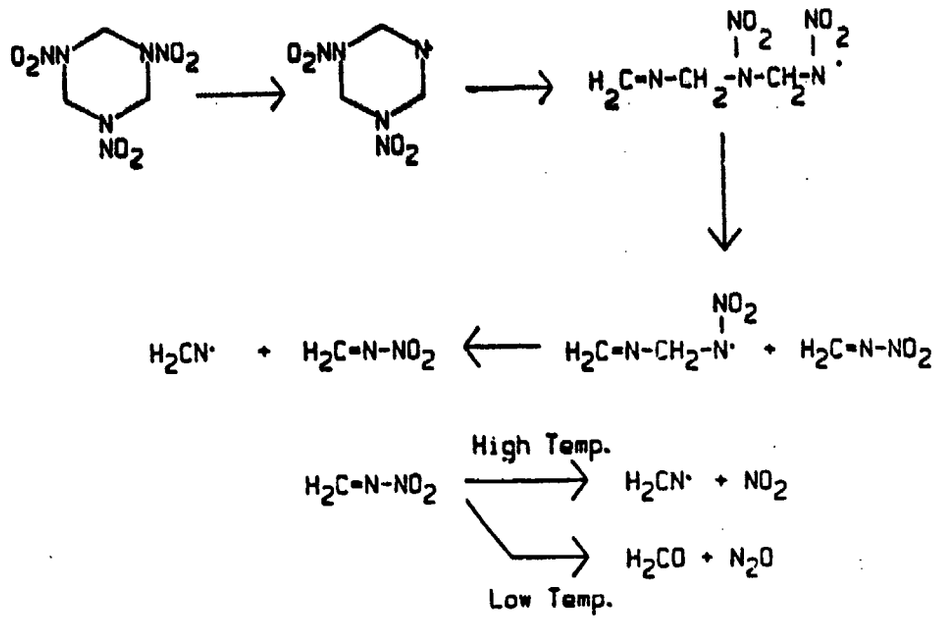
C. Chemical Mechanisms

Chemical Mechanisms Involved in the Uncatalyzed Decomposition of HMX and RDX. The ultimate goal of the present work involves reaching an understanding of the chemical mechanisms involved in borohydride catalysis of nitramine decomposition. However in order to accomplish this it will of course be necessary to understand the decomposition of uncatalyzed HMX and RDX as a baseline on which to base our understanding of the borohydride-catalyzed decomposition of these materials.

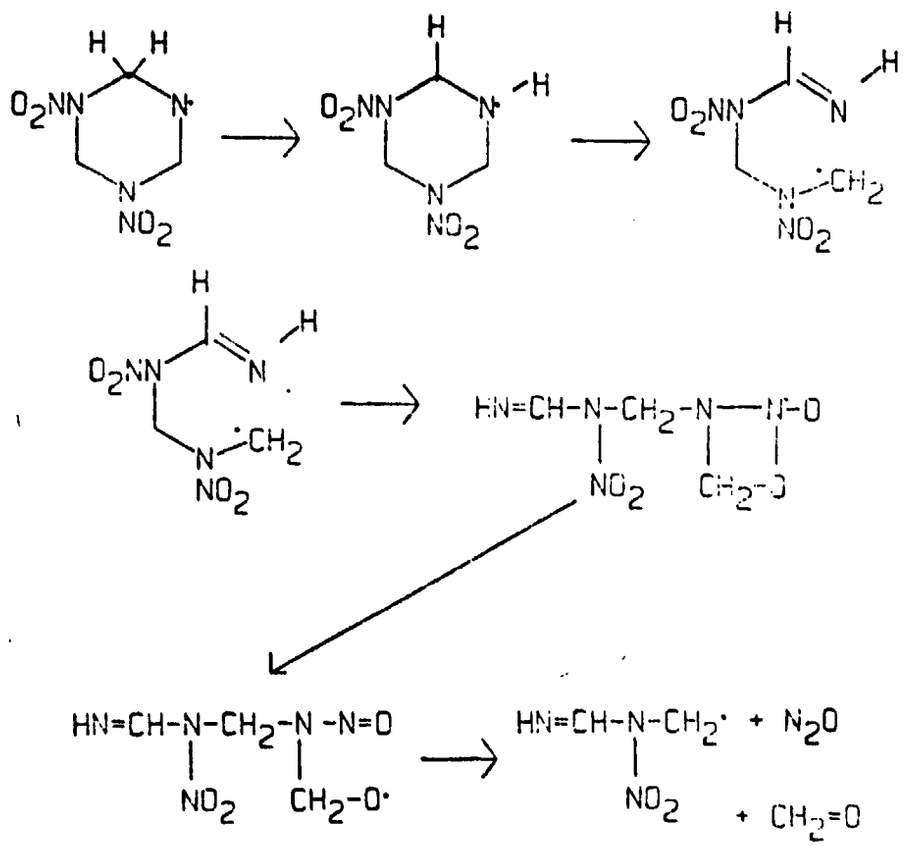
Note that the following discussion refers specifically to thermal decomposition and not to the ion fragmentation seen in mass spectrometers. The present writer generally thinks of RDX decomposition in the liquid phase as proceeding through a main pathway involving chemical mechanisms similar to the following (References 1-7; see especially References 4-6).

There is an observed tendency for formation of more HCN and NO_2 and less $H_2C{=}O$ and N_2O at higher temperatures and heating rates; this could possibly be understood[6] in terms of a shift between the pathways shown (Scheme I) for decomposition of $H_2C{-}N{-}NO_2$. Note that intermediacy of the N-nitroformimine $H_2C{=}N{-}NO_2$ is not necessary in order to account for the formation of N_2O and $H_2C{=}O$; these could also be formed by a mechanism such as that given in Scheme II.

Autoacceleratory behavior could occur through bimolecular followup reactions involving attack on hydrogen and oxygen by H· and other radical species[4,9,12,15] formed in the reaction, as shown in Schemes III and IV.



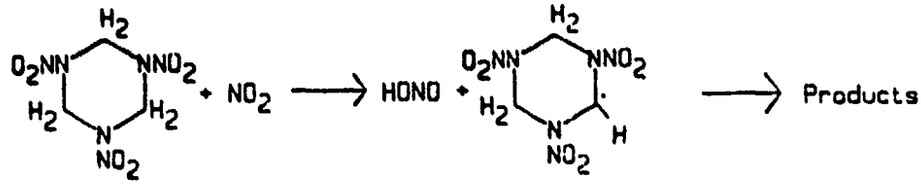
SCHEME I



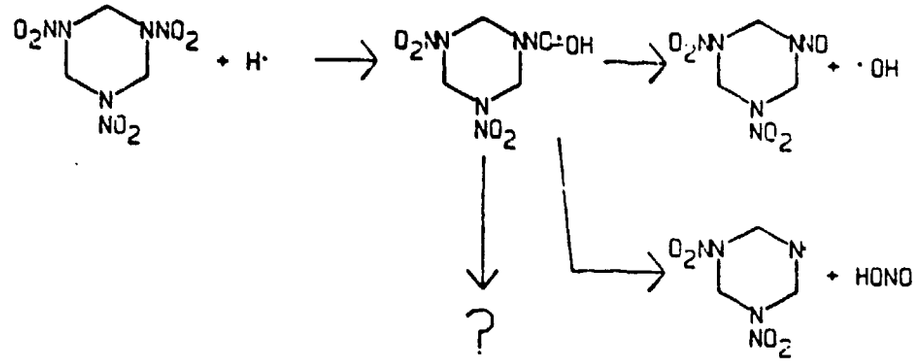
SCHEME II

Note however that Melius and Binkley have recently argued,[15] on the basis of BAC-MP4 MO calculations, that the formaldehyde and N_2O are not formed by the mechanisms of either Scheme I or Scheme II. They are uncertain as to the exact pathways by which these materials are formed. However their reaction schemes do include formation of NO_2 and H_2CN. via decomposition of $3H_2C{=}N{-}NO_2$) as shown in Scheme I above.

Furthermore, Zhao, Hintsa and Lee[14a] have studied RDX decomposition by infrared multiphoton dissociation and have reported that concerted pathways[4] (e.g., RDX ---> $3H_2C{=}N{-}NO_2$) are more important than has been heretofore suspected.

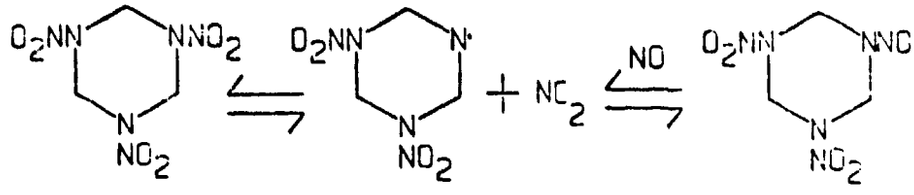


SCHEME III



SCHEME IV

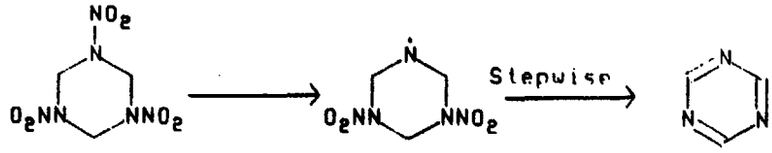
In addition to the pathway of Scheme IV, nitrosoamines could be formed via $N{-}NO_2$ cleavage and recombination with NO formed in the decomposition (Scheme V).



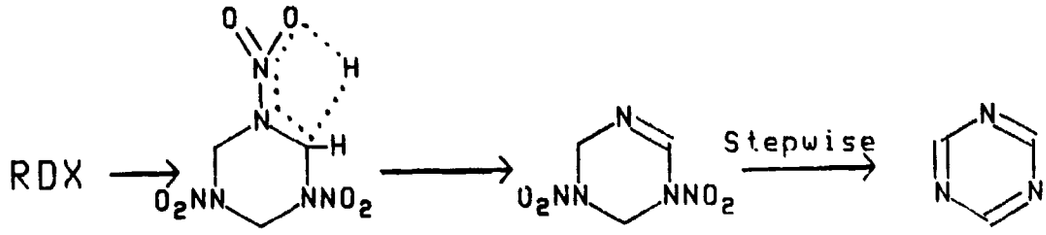
SCHEME V

The identification in the present work of 1,3,5-triazine seems of considerable interest because of its potential mechanistic significance. This significance arises because its presence indicates the occurrence of pathways not involving initial C-N cleavage; however these pathways could involve initial N-NO_2 cleavage, HONO elimination or H-abstraction by NO_2 or other radical species formed in the decomposition.

Possible mechanisms for formation of 1,3,5-triazine include: (a) formation via primary N-NO_2 cleavage (Scheme VI); (b) formation via primary HONO elimination (Scheme VII); (c) formation via initial abstraction of a hydrogen atom by NO_2 or some other radical species formed in the reaction (Scheme VIII); (d) formation via the nitroxide reported on the basis of ESR studies[16] (Scheme IX); and (e) trimerization of HCN formed in the decomposition of RDX (Scheme X).



SCHEME VI



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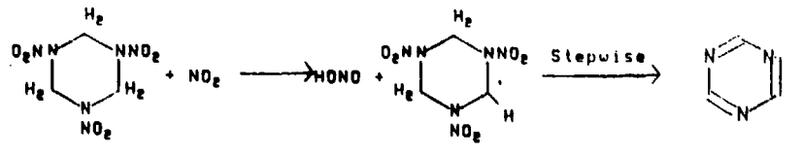

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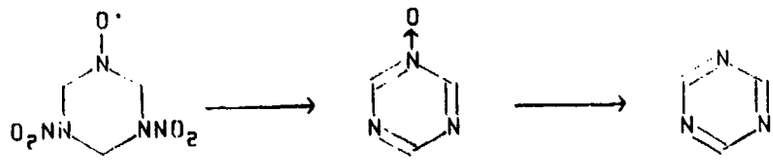

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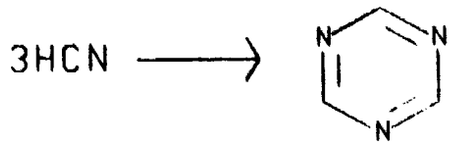

SCHEME X

Formation of triazine via trimerization of HCN should be considered but seems relatively unlikely, since trimerization of nitriles closely related to HCN, such as CH_3CN, appears to require[17] not only elevated temperatures but pressures in the range 8-10 kilobars and reaction times of hours (as opposed to 20 seconds in the present work).[17] HCN itself trimerizes under milder conditions, but acid catalysis is apparently required.[17] Note that some acid products such as HONO and HNO_3 can be formed in HMX and RDX decomposition.

However, it seems difficult to rule out HCN trimerization conclusively except by scrambling studies in mixtures of fully-ring-labeled and unlabeled RDX; we are presently planning to carry out such studies in connection with planned studies on $N-NO_2$ scrambling in decomposition of mixtures of fully-labeled and unlabeled RDX, both alone and in mixtures with borohydride salts. It is true that decomposition[18] of HMX (which does not possess a six-membered ring, but is known[4,6] to give HCN as a product of thermal decomposition) also gives 1,3,5-triazine. However, HMX would give 1,3,5,7-tetrazocine after loss of the elements of four molecules of HONO by pathways analogous to Schemes VI-VIII. By analogy with the known chemistry[19] of cyclooctatetraene, azocine and di- and triazocines (which are known[19] to yield respectively benzene and azabenzenes on thermolysis), it does not seem unreasonable to suppose that 1,3,5,7-tetrazocine might decompose further to 1,3,5-triazine.

The H-, HONO- and NO_2-stripping pathways shown in Schemes VI-VIII are presumably relatively minor pathways relative to the fragmentation pathways shown in Schemes I-IV. This follows from the small amounts (ca 5-10 percent) of 1,3,5-triazine (m/e 54 and 81) formed relative to m/e 44 (probably mainly N_2O and CO_2).

Possible Chemical Mechanisms Involved in Catalysis of HMX and RDX Decomposition by Borohydride Salts. It is possible to imagine at least three main types of initial pathways which might contribute to catalysis of HMX or RDX decomposition by borohydrides:

1. Decompostion of nitramine is initiated by direct reaction between nitramine and borohydride; for example by electron transfer, by attack of a B-H bond on nitro oxygen of the nitramine, or by a combination of these mechanisms.

2. An early decomposition product, for example NO_2, of the nitramine reacts with the catalyst to form products or intermediates, possibly free radicals, which react further with the nitramine, resulting in catalysis.

3. Unimolecular decomposition of the catalyst generates products or intermediates which react with nitramine, causing it to decompose faster than it otherwise would.

At present there is insufficient evidence to distinguish between these possibilities. Nevertheless, the following comments seem relevant.

A possible pathway of type (1) can be written based on a suggestion[20] contained in a Russian study of the reaction of a variety of nucleophilic reagents, including sodium borohydride ($NaBH_4$), with difluorodinitromethane, $CF_2(NO_2)$. The radicals produced were studied by ESR and trapping techniques, and identified as H· and $\cdot CF_2NO_2$. Their formation was rationalized in terms of the following mechanism:

$$CF_2(NO_2)_2 + BH_4^{\ominus} \longrightarrow CF_2(NO_2)_2^{\ominus} + H\cdot + BH_3$$

$$CF_2(NO_2)_2^{\ominus} \longrightarrow \cdot CF_2NO_2 + NO_2^{\ominus}$$

SCHEME XI

An analogous mechanism for catalysis of RDX decomposition by $K_2B_{12}H_{12}$ or $K_2B_{10}H_{10}$ might be written as follows:

$$RDX + B_{12}H_{12}^{\ominus} \longrightarrow RDX^{\ominus} + H\cdot + B_{12}H_{11}^{\ominus}$$

$$RDX + B_{12}H_{11}^{\ominus} \longrightarrow RDX^{\ominus} + H\cdot + B_{12}H_{10}$$

$$RDX^{\ominus} \longrightarrow \text{Products}$$

$$RDX + H\cdot \longrightarrow \text{Products}$$

SCHEME XII

Pathway (3) seems relatively unlikely, at least at lower temperatures; this is based on the apparent inertness[21] of salts closely related to $K_2B_{12}H_{12}$ when treated under conditions (200-500°C) as severe or more so than the 200-300°C temperatures which cause decomposition of HMX or RDX alone, and at which borohydride catalysis of HMX/RDX decomposition is observed. However it was reported[21] that above 505°C, $Na_2B_{12}H_{12}$ underwent exothermic thermal-oxidative degradation accompanied by a gain in weight equivalent to one oxygen atom per formula weight of the anhydrous salt, and that above 830°C it burned.

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Name

Organization

Address

City, State, Zip

(Remove this sheet, fold as indicated, staple or tape closed, and mail.)

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Director
U.S. Army Ballistic Research Laboratory
ATTN: SLCBR-DD-T
Aberdeen Proving Ground, MD 21005-5066

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UNITED STATES

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Director
U.S. Army Ballistic Research Laboratory
ATTN: SLCBR-DD-T
Aberdeen Proving Ground, MD 21005-9989

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